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by

L. R. Anderson, S. Maruyama, and R. E. Smalley

Chem. Phys. Letters (1990)

Rice University  
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Houston, Texas

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# ABSTRACT

Mass-selected silicon clusters were levitated in a Fourier transform ion cyclotron resonance mass spectrometer (FT-ICR), and monitored during chemisorption reaction with ethylene. The reactivity of the six positively charged clusters studied here varied sharply as a function of cluster size, indicating that ethylene is as sensitive a probe of the cluster surface chemistry as reported previously for ammonia. As with ammonia, the 39th and 45th clusters were found to be particularly unreactive towards ethylene chemisorption. The results suggest that most silicon clusters in this moderately large size range are able to anneal to an energetically most favored "crystalline" form.

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Ethylene Chemisorption on Levitated Silicon Cluster Ions:  
Evidence for the Importance of Annealing.

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ABSTRACT

Mass-selected silicon clusters were levitated in a Fourier transform ion cyclotron resonance mass spectrometer (FT-ICR), and monitored during chemisorption reaction with ethylene. The reactivity of the six positively charged clusters studied here varied sharply as a function of cluster size, indicating that ethylene is as sensitive a probe of the cluster surface chemistry as reported previously for ammonia. As with ammonia, the 39th and 45th clusters were found to be particularly unreactive towards ethylene chemisorption. The results suggest that most silicon clusters in this moderately large size range are able to anneal to an energetically most favored "crystalline" form.

Single crystal surface science depends critically on its ability to reproducibly prepare well-ordered periodic surface structures. For example, the recent STM studies by Avouris *et. al.*<sup>1</sup> of ammonia chemisorption on various sites of the 7x7 reconstruction of the (111) surface of silicon is particularly powerful because this surface structure is known and can be verified in detail. In the alternative cluster approach to surface science, where small clusters are to serve literally as "molecular models" of an idealized surface, it is also critical that well-ordered, known and verifiable structures be available. However, for many cluster systems where one can readily imagine a wide variety of structures of roughly equal stability, it is not clear that there need be any practical circumstance where a single structure dominates.

In the case of medium sized (20-60 atom) clusters of silicon, an intriguing result was obtained a few years ago by Elkind *et. al.*<sup>2</sup> when sharp variations were seen as a function of cluster size in reaction with ammonia. Whereas most silicon clusters were found to be quite reactive in ammonia chemisorption, those with clusters with 21, 25, 33, 39, and 45 atoms appeared to be relatively inert. At the time this was taken as evidence that the clusters had to a large extent "crystallized" to particular structural forms, some of which had few if any active sites for NH<sub>3</sub> chemisorption on their surfaces.

These ammonia chemisorption results have recently been verified in substantially more detail with a more elaborate version of the original cluster Fourier transform ion cyclotron resonance (FT-ICR) apparatus<sup>3,4</sup>.

Whereas it is clear for many clusters that multiple isomeric forms exist with different reactivities, clusters such as 39 and 45 appear to be dominated by a particularly unreactive, stable form. These results have stimulated a substantial level of activity within the theoretical community, with a number of structures being proposed together with supporting calculations<sup>6-11</sup>.

However, Jarrold and co-workers have recently reported a number of experiments with almost directly opposite results on these silicon clusters<sup>12</sup>. Using a tandem quadrupole apparatus with an intervening reaction region, they have examined the reactivity of positive silicon cluster ions with a variety of reagents such as ethylene<sup>12,13</sup> and oxygen<sup>14</sup>. Unlike the earlier FT-ICR studies, they observed nothing particularly different as a function of cluster size. More disturbingly, they observed extensive evidence for the presence of multiple isomers in abundance for all clusters. Most recently these experiments have been extended to reactions with ammonia where similarly confounding results were obtained<sup>15</sup>.

Stimulated by this controversy, we have examined the reactivity of positive silicon clusters to ethylene now that a new, greatly improved version of the cluster FT-ICR apparatus has become available. Remarkably, we still find special behavior. The results shown below indicate that ethylene is even more selective than ammonia in reactions with silicon cluster ions, with 39 and 45 still being special. The disagreement between the two types of apparatus is therefore real. We argue it is due to a difference in the conditions of formation and annealing of the clusters prior to reaction.

## EXPERIMENTAL

Silicon clusters were prepared by laser-vaporization of a silicon disc in a supersonic nozzle and injected as singly-charged positive ions into the trap of a specially designed FT-ICR apparatus. This new apparatus differed from previous versions in our laboratory<sup>2,3</sup> in two critical areas. First the supersonic cluster source was replaced with a newly developed cluster "minisource" sketched in cross-section in Figure 1. Here a fast pulsed valve of the "current loop" type<sup>16</sup> is mounted in one arm of a standard UHV six-way conflat cross (4" bore ID.). As shown in Fig. 1 a laser-vaporization nozzle assembly is bolted to the end of this pulsed nozzle. For the experiments described below this nozzle was operated with a 125 microsecond pulse duration with a flow of  $0.07 \text{ cm}^3 \text{ atm}$  per pulse, and the Nd:YAG 2nd harmonic vaporization laser (15-20 mJ focussed to a 0.1 cm diameter spot) was timed to hit the silicon target disk roughly 60 microseconds up the rising edge of the gas pulse. As shown in the nozzle detail of Fig. 1, the laser-ejected plume of silicon plasma was allowed to swirl into a 0.3 cm diameter, 1 cm long partially confined volume which we have come to call the "waiting room". Here the silicon clusters were allowed to thermalize and grow for about 40 microseconds as fresh, cool helium carrier gas continued to flow in from the pulsed nozzle. The subsequent supersonic expansion was directed by a 2 cm long  $10^\circ$  cone, the central portion of the jet being skimmed by a 0.2 cm dia. orifice electroformed skimmer. Even though this cluster minisource is less than one tenth the size of our previous sources, and pumped by only a single  $170 \text{ l s}^{-1}$  turbopump, we find it produces roughly the same cluster beam intensity, with far better reproducibility and control.

The second major difference from the previous cluster ICR experiments was that we switched to direct injection of the supersonic cluster beam into the FT-ICR trap. Remarkably, this turns out to work perfectly without any guiding ion optics at all. Trajectory calculations reveal that *all* ions in the 10 milliradian divergence supersonic cluster ion beam passing through the skimmer transit smoothly through the fringing field of the 6 Tesla superconducting magnet and into the ICR cell. A small pulsed deceleration field is used to select the mass range of clusters to be trapped. The result of these two changes in our previous design is that FT-ICR experiments on levitated clusters are now sufficiently straightforward to be a standard technique in chemistry and physics. A more extensive description of this apparatus and its performance will appear elsewhere<sup>17</sup>.

## RESULTS AND DISCUSSION

Figure 2 displays the FT-ICR mass spectrum of silicon clusters as they appear initially after injection via the supersonic cluster beam. Since the full supersonic beam travels through the ICR each injection pulse, there is a substantial pressure of helium present in the cell during injection and for a short time afterward as the  $170 \text{ l s}^{-1}$  turbopumps on either end of the magnet pump the cell back down. For the experiments discussed here, typically 50 successive supersonic cluster beam pulses were accumulated in the ICR cell prior to measurement at  $10 \text{ pulses s}^{-1}$ . We estimate the average helium pressure in the cell during these first 5-6 seconds of the cell loading process to be  $10^{-4}$  torr.



Since the cluster ions are all accelerated by the supersonic expansion to near the terminal beam velocity of  $1.9 \times 10^5 \text{ cm s}^{-1}$ , they have a translational energy linearly proportional to their mass. In the case of  $\text{Si}_{45}^+$ , for example, this is roughly 24 eV. In order to trap such clusters we removed sufficient energy with a pulsed decelerator just before the clusters entered the ICR trap so that they were unable to pass the rear door electrode which was held at +10 volts. The clusters were trapped by switching the potential of a "screen" door at the front of the trap to +10 volts a few tens of microseconds after the new cluster packet passed by. This injection process therefore leaves the silicon clusters bouncing back and forth in the ICR cell with up to 10 eV translational energy. Collisions with the helium background gas scattered out of the supersonic beam begin the process of randomizing this axially-directed translational energy into motion along the other two spatial directions. Even if the silicon cluster ions have been extensively cooled internally by the supersonic expansion, the effect of these collisions immediately following the injection process will initially be to heat them up to over 300K. In fact with the rather mild supersonic expansion conditions we have employed to generate these cluster ion beams, the clusters are unlikely to be strongly cooled. Initially their internal temperatures as they approach the ICR trap may be well above 400K and the initial effect of collisions will be to heat them further.

In this version of the cluster ICR apparatus the cell walls were held at room temperature. To ensure the clusters were well thermalized in the ICR trap we typically exposed them to argon at a pressure of  $2 \times 10^{-5}$  torr for an additional 10 seconds. The FT-ICR mass spectrum shown in Fig. 2 was recorded after an additional 10 second pumping time (the turbopumps now aided by a

cryopump previously valved off under computer control) to allow the ICR cell background gas pressure to fall below  $5 \times 10^{-8}$  torr. The fine structure seen in each main peak in the mass spectrum is due to the various isotopomers arising from the  $\text{Si}^{28}$ ,  $\text{Si}^{29}$ , and  $\text{Si}^{30}$  isotopes in natural abundance.

Since the mass of ethylene is the same as the dominant isotope of silicon, it was necessary to sweep away some of the clusters to generate a clear baseline. As shown in Fig. 3, we elected in this case to sweep out all but  $\text{Si}_{36}^+$ ,  $\text{Si}_{39}^+$ ,  $\text{Si}_{42}^+$ ,  $\text{Si}_{45}^+$ ,  $\text{Si}_{48}^+$ , and  $\text{Si}_{51}^+$ . As has been discussed in other papers from this group<sup>3,4</sup>, our preferred technique here is known in the ICR community as "SWIFT" (stored waveform inverse fourier transform)<sup>18</sup>. As is evident from careful inspection of the remaining peaks in Fig. 3, we chose the SWIFT waveform to leave behind slightly different isotopomer distributions for each cluster so that their subsequent reaction products could be more readily traced.

Our central result is evident in Figure 4. This is the FT-ICR mass spectrum obtained by taking the SWIFTed cluster distribution shown in Fig. 3 and exposing those clusters to ethylene at a pressure of  $1 \times 10^{-5}$  torr for a period of 20 seconds -- sufficient time for the average cluster to have experienced roughly 5,000 collisions with ethylene molecules. Note that there is evidence for some reaction on all the silicon clusters, but it is clear that silicon clusters with 36, 42, and 51 atoms are considerably more reactive than those with 39, 45, or 48 atoms. This result is highly reproducible. The experiment was repeated with a wide range of thermalization conditions prior to exposure to the ethylene reactant. Basically the same result was obtained when the argon thermalization period was varied throughout the range of 0 to

over 10,000 collisions. In some experiments the clusters were allowed to thermalize as they were levitated in the trap for a period of over 100 seconds. This should have been sufficiently long for effective cooling by infrared emission alone, even in the absence of collisions. We are confident, therefore, that the observed special reactivity behavior is characteristic of the ground electronic state of the clusters at an internal temperature of near 300K.

Figure 5 shows the result of a subsequent exposure of these clusters after the chemisorbed products of the first reaction experiment shown in Fig. 4 were ejected by an appropriate SWIFT waveform. Note that the bare silicon clusters that had survived the initial ethylene exposure are now considerably less reactive, and the clusters at 39, 45, and 48 are relatively more prominent. This is evidence that multiple geometrical isomers were present to some extent in the initial cluster distribution. Further exposure to ethylene continued to sort the clusters out in accord with their relative reactivity. By the end of 40,000 collisions (which is near the maximum allowed by diffusional loss of the cluster ions from the ICR cell) the only remaining clusters detectable in this mass range were  $\text{Si}_{39}^+$ ,  $\text{Si}_{45}^+$ , and (least intense)  $\text{Si}_{48}^+$ .

These ethylene chemisorption experiments confirm our earlier evidence that certain clusters such as  $\text{Si}_{39}^+$  and  $\text{Si}_{45}^+$  can take structural forms which are specially unreactive. The new data also show that  $\text{Si}_{48}^+$  is rather unreactive as well. Since  $\text{Si}_{48}^+$  was not evidently special in the earlier experiments with ammonia<sup>2-4</sup>, we made a quick check with the new apparatus to see if this was really due to a difference in the way the two reagents sense

the  $\text{Si}_{48}^+$  cluster surface. A new set of ammonia reaction experiments confirmed that the dominant structural isomers of  $\text{Si}_{39}^+$  and  $\text{Si}_{45}^+$  are relatively unreactive toward ammonia chemisorption, while  $\text{Si}_{48}^+$  does ultimately react away. We suspect the variation in apparent reactivity of ethylene and ammonia on the surface of  $\text{Si}_{48}^+$  is more a quantitative than a qualitative difference. In general for all silicon clusters ammonia is simply more reactive than ethylene. A similar example is provided by water, which on silicon clusters in the FT-ICR apparatus is even more reactive than ammonia. Although in the initial work from this group<sup>2</sup> it appeared that water was not selective in its reactions with the silicon clusters, more careful experiments with the new apparatus now show that water (in small amounts) actually is somewhat selective, with the 39 and 45 clusters again being the least reactive. However,  $\text{H}_2\text{O}$  is sufficiently aggressive that all clusters ultimately do react.

We are currently checking to see if this same behavior occurs for the extremely reactive gas, NO, which like water seemed to react unselectively with all silicon cluster ions in the original ICR experiment<sup>2</sup>. In quick survey experiments we have recently carried out with positive germanium clusters<sup>19</sup>, NO was the only reagent for which reactions were seen. Intriguingly, the least reactive germanium clusters with NO were  $\text{Ge}_{39}^+$  and  $\text{Ge}_{45}^+$ . Earlier photofragmentation experiments from this group<sup>20</sup> had led to the suggestion that the structures of the germanium clusters in this size range were similar to those of silicon. These new ICR results are beginning to support that notion.

## THE IMPORTANCE OF ANNEALING

The disagreement between the FT-ICR experiments in this laboratory and those of Jarrold and co-workers is therefore even sharper than before. We continue to find evidence for special chemisorption behavior of certain silicon clusters, not only with ammonia, but with a variety of reagents. On the other hand, the tandem quadrupole experiments of the Jarrold group have never shown any clusters in this region to be special. We believe this difference is most likely due to an actual difference in the clusters themselves. Somehow the clusters in our experiment have been able to anneal into energetically favored structures, whereas those in Jarrold's apparatus have for some reason become trapped in a fairly large set of less well-ordered structures.

The difference may be in the cluster sources. Our pulsed minisource forms the clusters in the early stages of nucleation from the laser-generated vapor where growth is predominantly by sequential addition of single atoms. Most of this growth occurs during the first few tens of microseconds while the carrier gas is still quite hot from the laser pulse. The clusters may stay hot enough in such a source to anneal while they grow. On the other hand, the laser-vaporization cluster source used by Jarrold's group forms the clusters on a much longer time scale (milliseconds) in a slowly moving low pressure helium gas, efficiently cooled by thermal conduction to the walls of the source. During this longer time interval the majority of the silicon is in the form of clusters (since most of the free silicon atoms will have diffused preferentially to the walls). In such a source cluster growth will rapidly be dominated by aggregation of small and medium-sized clusters with

each other. Without significant reheating, these cluster aggregates may never be able to anneal to a single most energetically favored form.

Alternatively, it may be that the difference in the clusters between the two experiments occurs because of the much longer time scale available for annealing as the clusters are injected and accumulated in the FT-ICR trap (seconds), as opposed to the far shorter time scale available in the tandem quadrupole apparatus (milliseconds). Here the issue involves both the question of the required temperature for annealing and the required cooling schedule. In both cases the ICR apparatus has advantages, but it will be a while yet before it is known which of these -- if any -- explains the remarkably persistent differences in silicon cluster behavior between the two laboratories.

In the early days of single crystal surface science it was necessary to learn the art of preparing clean, uniform surfaces with a single well-known structure. The new FT-ICR results discussed above provide basis for some optimism that such an art may be developed for individual silicon clusters. Although most of the  $\text{Si}_{39}^+$  and  $\text{Si}_{45}^+$  injected into the ICR trap in these experiments appears to be in the specially inert form, there is clearly a significant contingent of other, more reactive forms present. It will be interesting to see how effectively these can be annealed away. Either by annealing, or simply by titrating away the reactive forms, it may be possible to reliably generate a sample of levitated silicon clusters in ultrahigh vacuum which consists purely of identical, single cluster "crystals".

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#### FIGURE CAPTIONS

Figure 1. Schematic of new supersonic cluster beam "minisource".

Figure 2. FT-ICR mass spectra of positive silicon cluster ion distribution directly injected from the supersonic minisource, levitated in a high vacuum by a 6 tesla magnetic field, trapped by weak electrostatic fields, and thermalized to 300K.

Figure 3. Silicon cluster distribution after selective removal of some ions from the cell by a "SWIFT" excitation.

Figure 4. FT-ICR mass spectrum of the SWIFTed silicon clusters after exposure to  $10^{-5}$  torr ethylene for 20 seconds -- roughly 5,000 collisions.

Figure 5. FT-ICR mass spectrum after SWIFT ejection of the reaction products seen in Fig. 4, followed by a second 5,000 collision exposure to ethylene.









